Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1968). **B24**, 1701

The use of neutron anomalous scattering in crystal-structure analysis. II. Centrosymmetric structures.

By A. K. Singh and S. Ramaseshan, *Material Sciences Division, National Aeronautical Laboratory Bangalore-17, India*

(*Received* 19 *April* 1968 *and in revised form* 5 *August* 1968)

The methods for locating the positions of the anomalous scatterers in a centrosymmetric structure and determining the signs of the reflexions using the data collected at two neutron energies are given. The results are general and can be used for X-ray anomalous scattering as well.

In an earlier publication (part I, Singh & Ramaseshan, 1968*a*) the authors have suggested a method of locating the position of the anomalous scatterers and determining the phases of the non-centrosymmetric structure factors using the data collected at two neutron energies. A similar approach for centrosymmetric structures is reported in this communication.

The notation used here is the same as in part I (Singh & Ramaseshan, 1968*a*).

Location of the anomalous scatterers

Let us consider a centrosymmetric structure containing n_A identical anomalous scatterers with their scattering lengths of the form $b_0+b'+ib''$ and n_N normal scatterers. The structure factor is given by

$$F(\mathbf{H})=F_N(\mathbf{H})+F_A(\mathbf{H})+iF''_A(\mathbf{H})$$
$$=\mathscr{F}(\mathbf{H})+iF''_A(\mathbf{H}) \tag{1}$$

where

$$\mathscr{F}(\mathbf{H})=F_N(\mathbf{H})+F_A(\mathbf{H})$$
$$F_A(\mathbf{H})=b(r)\mathbf{x}$$
$$F''_A(\mathbf{H})=b(i)\mathbf{x}$$
$$\mathbf{x}=2\sum_{j=1}^{n_A}\cos 2\pi\mathbf{H}\,.\,\mathbf{r}_{Aj}\exp\left[-\left(B_{Aj}\,.\,\frac{\sin^2\theta}{\lambda^2}\right)\right]$$
$$F_N(\mathbf{H})=2\sum_{j=1}^{n_A} b_{Nj}\cos 2\pi\mathbf{H}\,.\,\mathbf{r}_{Nj}\exp\left[-B_{Nj}\frac{\sin^2\theta}{\lambda^2}\right].$$

Following the procedure indicated in an earlier publication (Singh & Ramaseshan, 1968*a*), equation (1) can be rewritten for two neutron energies E_1 and E_2 as follows:

$$|F_N(H)|^2+2b_1(r)\mathbf{x}F_N(\mathbf{H})+\{b_1^2(r)+b_1^2(i)\}|x|^2-|F_1(H)|^2=0 \tag{2}$$

$$|F_N(H)|^2+2b_2(r)\mathbf{x}F_N(\mathbf{H})+\{b_2^2(r)+b_2^2(i)\}|x|^2-|F_2(H)|^2=0 \tag{3}$$

On eliminating $|F_N(H)|^2$ between (2) and (3) and noting that $[\mathbf{x}F_N(\mathbf{H})]^2=|x|^2|F_N(\mathbf{H})|^2$ we get

$$P|x|^4-2Q|x|^2+R=0\,, \tag{4}$$

where

$$P=\{b_1(r)-b_2(r)\}^2[2\{b_1^2(i)+b_2^2(i)\}+\{b_1(r)-b_2(r)\}^2]+\{b_1^2(i)-b_2^2(i)\}^2$$

$$Q=\{b_1(r)-b_2(r)\}^2[|F_1(H)|^2+|F_2(H)|^2]+\{b_1^2(i)-b_2^2(i)\}\,[|F_1(H)|^2-|F_2(H)|^2]$$

$$R=\{|F_1(H)|^2-|F_2(H)|^2\}^2.$$

Equation (5) can be obtained from equation (14) of Singh & Ramaseshan (1968*a*) by letting $|F_{m1}(H)|^2=|F_1(H)|^2$, $|F_{m2}(H)|^2=|F_2(H)|^2$ and $\delta=0$.

The roots of equation (5) are

$$|x_\pm|^2=\frac{Q}{P}\pm\left[\frac{Q^2}{P^2}-\frac{R}{P}\right]^{1/2}. \tag{5}$$

Thus for a given set of values of $|F_1(H)|^2$ and $|F_2(H)|^2$ two values of $|x|^2$ and $|F_N(H)|^2$ are possible. To understand the physical significance of the two roots let us consider a case with $b_1(i)=b_2(i)=0$; equation (5) then gives

$$|x_+|^2=\{|F_1(H)|+|F_2(H)|\}^2/\{b_1(r)-b_2(r)\}^2 \tag{6a}$$

$$|x_-|^2=\{|F_1(H)|-|F_2(H)|\}^2/\{b_1(r)-b_2(r)\}^2 \tag{6b}$$

Further, writing equation (1) for two neutron energies and subtracting one from the other we have for $b_1(i)=b_2(i)=0$

$$F_1(\mathbf{H})-F_2(\mathbf{H})=\{b_1(r)-b_2(r)\}\mathbf{x}$$

or

$$|F_1(H)|S(F_1)-|F_2(H)|S(F_2)=\{b_1(r)-b_2(r)\}\mathbf{x}\,. \tag{7}$$

$S(F_1)$ and $S(F_2)$ are the signs of $F_1(\mathbf{H})$ and $F_2(\mathbf{H})$. It is well to note that if $b_1(i)$ and $b_2(i)$ are not zero, $F_1(\mathbf{H})$ and $F_2(\mathbf{H})$ have phases different from 0 and π. In such cases we can only talk of the signs of $\mathscr{F}_1(\mathbf{H})$ and $\mathscr{F}_2(\mathbf{H})$.

On comparing equation (7) with (6*a*) and (6*b*) we find that $|x_+|^2$ and $|x_-|^2$ are the correct solutions for the cases $S(\mathscr{F}_1)\neq S(\mathscr{F}_2)$ and $S(\mathscr{F}_1)=S(\mathscr{F}_2)$ respectively.

It can be easily shown that $S(\mathscr{F}_1)\neq S(\mathscr{F}_2)$ occurs when

$$S(N)\neq S(x)$$

and

$$|b_1(r)\mathbf{x}|>|F_N(H)|>|b_2(r)\mathbf{x}|$$

for

$$b_1(r)>b_2(r)\,. \tag{8}$$

In the case of X-ray anomalous scattering the changes in scattering factors due to change in wavelength are not large and therefore the reflexions with $S(\mathscr{F}_1)\neq S(\mathscr{F}_2)$ will be very weak. In the case of neutron anomalous scattering these changes may be quite large. In such cases the reflexions with $S(\mathscr{F}_1) \neq S(\mathscr{F}_2)$ may be strong but the number of such reflexions is limited owing to the small probability of condition (8) being satisfied. Thus $|x_-|^2$ will represent the correct roots for most reflexions. The change of sign however can occur more frequently if scattering length for one of the energies, say E_2, is negative [*i.e.* $b_2(r)$ is negative and further for the sake of discussion we shall assume again that $b_2(r) < b_1(r)$]. The conditions to be satisfied for such a change are

$$|b_2(r)\mathbf{x}| > |F_N(H)| \quad \text{if} \quad S(N) = S(x)$$

or

$$|b_1(r)\mathbf{x}| > |F_N(H)| \quad \text{if} \quad S(N) \neq S(x) .$$

In practice it seems advantageous to choose the neutron energies such that $b_1(r)$ and $b_2(r)$ are of the same sign.

For structures with large 'heavy atom' ratio, the position of the anomalous scatterer can be determined by an ordinary Patterson synthesis or synthesis with $|F_1(H)|^2 + |F_2(H)|^2$ (Ramaseshan, 1966). The latter is known to contain only $A-A$ and $N-N$ vectors if the neutron energies are chosen so that $b_1(r) = -b_2(r)$. As the 'heavy atom' ratio decreases, an increasing background is provided by the $N-N$ vectors. For a small 'heavy atom' ratio, $A-A$ vectors can hardly be distinguished from the $N-N$ vectors. It is in such cases that the present method is particularly useful. Further for a structure with small 'heavy atom' ratio, cases with $S(\mathscr{F}_1) \neq S(\mathscr{F}_2)$ are not many and $|x_-|^2$ represents the correct root for most reflexions.

Equation (4) has coincident roots if E_1 and E_2 are chosen so that $b_1(r) = b_2(r)$ and $b_1(i) \neq b_2(i)$. The roots are then given by

$$|x_+|^2 = |x_-|^2 = Q/P .$$

Thus there is no ambiguity in the determination of $|x|^2$. However in such a case the signs of the reflexions cannot be determined [see equation (9)].

A Patterson synthesis with $b_1^2(r)\,|x_-|^2$ as coefficients will yield the positions of the anomalous scatterers. A comparison of the calculated $|x|^2$ values with those obtained from equation (4) will indicate the cases in which a wrong solution has been chosen. Once such corrections have been made $|x_-|^2$ values from equation (4) can be used to refine the thermal and the positional parameters of the anomalous scatterers.

The sign determination

On subtracting equation (3) from (2) we get,

$$2F_N(\mathbf{H})\,\{b_1(r) - b_2(r)\}\mathbf{x} = \{|F_1(H)|^2 - |F_2(H)|^2\} - [\{b_1^2(r) + b_1^2(i)\} - \{b_2^2(r) + b_2^2(i)\}]\,|x|^2 . \quad (9)$$

Thus, x being known, $F_N(\mathbf{H})$ can be determined. With this all the information necessary for solving a structure is complete. A Fourier synthesis with $F_N(\mathbf{H})$ as coefficients will reveal the position of the normal scatterers.

As pointed out in the previous section, the choice of two neutron energies such that $b_1(r) = b_2(r)$ and $b_1(i) \neq b_2(i)$ leads to unique solution of $|x|^2$. However on letting $b_1(r) = b_2(r)$ in equation (9) the term containing $F_N(\mathbf{H})$ vanishes and equation (9) becomes an identity. Thus $F_N(\mathbf{H})$ cannot be determined under these conditions. However, from equation (2) or (3), both of which are identical under the condition $b_1(r) = b_2(r) = b(r)$, we get

$$|F_N(\mathbf{H})| = -b(r)\mathbf{x} \pm [b^2(r)|x|^2 + \{|F_1(H)|^2 - (b_1^2(r) + b_1^2(i))\,|x|^2\}]^{1/2} .$$

These two roots correspond to the two cases (i) $F_N(\mathbf{H})$ having the same sign as $b(r)\mathbf{x}$ and (ii) $F_N(\mathbf{H})$ having a sign opposite to that of $b(r)\mathbf{x}$. However this ambiguity cannot be resolved.

Thus an attempt to combine the data at two neutron energies to give $|x|^2$ leads to two possible solutions [equation (5)]. The correct roots can be chosen indirectly and a Patterson synthesis with these will give the position of the anomalous scatterers. Equation (9) can then be used to determine $F_N(\mathbf{H})$.

Equation (6) leads to a unique solution for $b_1(r) = b_2(r)$ and $b_1(i) \neq b_2(i)$ but $F_N(\mathbf{H})$ cannot be determined from equation (9). This situation is similar to that encountered in the noncentrosymmetric case (Singh & Ramaseshan, 1968*b*) wherein such a choice of radiation gives $|x|^2$ unambiguously but the ambiguity in the phase remains unresolved.

References

RAMASESHAN, S. (1966). *Curr. Sci.* **35**, 87.
SINGH, A. K. & RAMASESHAN, S. (1968*a*). *Acta Cryst.* B**24**, 35.
SINGH, A. K. & RAMASESHAN, S. (1968*b*). *Acta Cryst.* B**24**, 881.

Acta Cryst. (1968). B**24**, 1702

The crystal structure of iodine monobromide, IBr.

By L. N. SWINK AND G. B. CARPENTER, *Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island* 02912, *U.S.A.*

(*Received* 29 *August* 1968)

An addendum to *Acta Cryst.* (1968), B**24**, 429.

In an earlier article under this title (Swink & Carpenter, 1968) we neglected, through an oversight, to refer to a more recent powder diffraction study (Cheesman & Hawes, 1959) covering the entire composition range of iodine–bromine mixtures. The discrepancy between the cell constants reported in the latter paper for a 50 at.% powder and those reported by us for single crystals of the same composition remains unexplained, despite rechecking of original photographs in both laboratories (Cheesman, 1968).

References

CHEESMAN, G. H. (1968). Private communication.
CHEESMAN, G. H. & HAWES, L. L. (1959). *Acta Cryst.* **12**, 142.
SWINK, L. N. & CARPENTER, G. B. (1968). *Acta Cryst.* B**24**, 429.